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PHOTOLYSIS OF  $O_3$  AT 3130A

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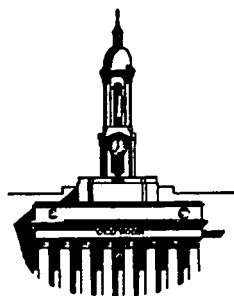
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and M. Nicolet

November 1, 1972

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IONOSPHERE RESEARCH LABORATORY



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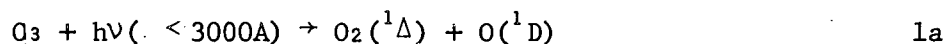
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## ABSTRACT

The photolysis of  $O_3$  at 3130Å and 25°C has been studied in the presence of a large excess of  $N_2O$  to react with any  $O(^1D)$  atoms produced. From the  $N_2$  produced, the quantum efficiency for  $O(^1D)$  production was found to be  $0.50 \pm 0.03$ .

Much of the solar radiation absorbed by the ozone in the stratosphere is in the range of 3000-3400Å. Consequently, it is important to know the nature of the primary fragments produced in O<sub>3</sub> photolysis in this wavelength range if one is to understand the complex chemistry in the O<sub>3</sub> layer.

The photolysis of O<sub>3</sub> in the range of 2200-3000Å, mainly at 2537Å, has been extensively studied.<sup>1</sup> It is now accepted that the primary process is



The electronically excited species react with O<sub>3</sub> as follows



where O<sub>2</sub>\* is one of the high-lying electronic states of O<sub>2</sub> (or even two O(^3P) atoms, in which case reaction 5 is unnecessary). The rate coefficient ratio  $k_{3a}/k_3 = 0.75 \pm 0.25$  where  $k_3 \equiv k_{3a} + k_{3b}$ .<sup>1</sup>

The dissociation enthalpy of O<sub>3</sub> at 0°K can be computed to be 24.2 kcal/mole from thermodynamic data.<sup>2</sup> From spectroscopic data, the electronic excitation energy in O<sub>2</sub>(<sup>1</sup>Δ) and O(<sup>1</sup>D) is 20.8 and 45.4 kcal/mole, respectively. Thus for wavelengths > 3160Å, there is insufficient energy (i.e. < 90.4 kcal/mole) for reaction 1a to occur. The other possible primary processes are



Whereas primary process 1a leads to a quantum yield of  $O_3$  disappearance,  $-\phi\{O_3\}$ , of  $5.5 \pm 0.5$ , processes 1b, 1c, and 1d predict  $-\phi\{O_3\} = 3.5 \pm 0.5$ , 2.0, and 4.0, respectively.

Two groups have investigated the photodecomposition at 3340Å by monitoring  $-\phi\{O_3\}$ . Castellano and Schumacher<sup>3</sup> found  $-\phi\{O_3\} = 4.0$ , and Jones and Wayne<sup>4,5</sup> found  $-\phi\{O_3\} = 3.6 \pm 0.4$ . Furthermore Jones and Wayne<sup>5</sup> added  $H_2$ , found no increase of  $-\phi\{O_3\}$ , and concluded that  $O(^1D)$  was not produced. Thus the sole primary process at 3340Å is reaction 1d.

Presumably the primary process changes from reaction 1a to reaction 1d near the energy threshold at 3160Å. Thus at 3130Å both processes may be occurring. The gas phase photolysis has been studied at 3130Å by Castellano and Schumacher<sup>6</sup> and Jones and Wayne.<sup>4,5</sup> Both groups monitored  $-\phi\{O_3\}$ , but the two groups obtained conflicting results. The former investigators found  $-\phi\{O_3\} = 6.0$  and concluded that reaction 1a was the sole reaction, whereas the latter investigators found  $-\phi\{O_3\}$  to be close to 4.0 and concluded that reaction 1d must be dominant. However Jones and Wayne<sup>5</sup> did add  $H_2$ , and found an enhancement in  $-\phi\{O_3\}$ , so that some  $O(^1D)$  must be produced.

Three studies have also been made in condensed phases at 3130Å. Taube<sup>7</sup> studied the reaction in  $H_2O$ , whereas DeMore and Raper<sup>8,9</sup> studied the reaction in liquid Ar at 87°K. In these studies the efficiency of  $O(^1D)$  production was monitored in three different ways. The results were all similar and DeMore and Raper<sup>9</sup> concluded that the efficiency of  $O(^1D)$  production was  $0.4 \pm 0.15$ .

It is clear that the primary process at 3130Å in the gas phase is not yet established. Therefore we have measured the efficiency of  $O(^1D)$  production at room temperature by photolyzing  $O_3$  in the presence of excess

$\text{N}_2\text{O}$ . These experiments are similar to those of Goldman et al.<sup>10</sup> The only additional reactions are



The quantum efficiency for  $\text{O}(^1\text{D})$  production,  $\phi\{\text{O}(^1\text{D})\}$ , is given by

$$\phi\{\text{O}(^1\text{D})\} = \phi\{\text{N}_2\}(k_6/k_{6a})(1 + k_3[\text{O}_3]/k_6[\text{N}_2\text{O}]) \quad \text{I}$$

Thus the measurement of  $\phi\{\text{N}_2\}$  will give  $\phi\{\text{O}(^1\text{D})\}$  providing  $k_6/k_{6a}$  and  $k_3/k_6$  are known. The ratio  $k_6/k_{6a}$  has been measured carefully.<sup>11,12</sup> For translationally equilibrated  $\text{O}(^1\text{D})$  atoms, as would be produced here,  $k_6/k_{6a} = 2.1$ . For thermal  $\text{O}(^1\text{D})$  atoms,  $k_3/k_6$  is about 4.<sup>1,10</sup> This value is not very accurately known, but since  $[\text{O}_3] \ll [\text{N}_2\text{O}]$ ,  $k_3[\text{O}_3]/k_6[\text{N}_2\text{O}]$  contributes only slightly to the calculation.

The experimental procedure was similar to that of Goldman et al.<sup>10</sup> The 3130A radiation was obtained from a 400 watt Hanovia medium pressure lamp. The radiation passed through an interference filter centered at 3150A with a 120A half-band-width. To be sure that the Hg line at 3020A was not contributing to the photolysis, the extinction coefficient for  $\text{O}_3$  was measured and it agreed with that at 3130A. No more than 10% of the absorbed radiation could be at 3020A. Actinometry was obtained by measuring the  $\text{N}_2$  produced in the photolysis of  $\text{CH}_3\text{N}_2\text{CH}_3$  at matched absorbance, using an RCA 935 phototube to measure the absorbance.  $\phi\{\text{N}_2\}$  is known to be 1.0 in the  $\text{CH}_3\text{N}_2\text{CH}_3$  photolysis.<sup>13</sup> Some  $\text{N}_2$  was produced in unirradiated  $\text{N}_2\text{O}-\text{O}_3$  mixtures, but this was only 5-10% of that produced during irradiation. Corrections for this background  $\text{N}_2$  were made.

The results of the experiments are shown in Table I. It can be seen that  $\phi\{\text{O}(^1\text{D})\}$  is  $0.50 \pm 0.03$  in good agreement with the liquid phase results.<sup>7-9</sup> Presumably at 3130A, the primary process is 50% reaction 1a

and 50% reaction  $\text{ld}$ . If so the predicted value for  $-\dot{\Phi}\{\text{O}_3\}$  is  $4.8 \pm 0.2$ . This value lies exactly between those found by Jones and Wayne<sup>4,5</sup> and Castellano and Schumacher.<sup>6</sup>

A value of 0.50 for the quantum efficiency at 3130A is an indication that there is production of  $\text{O}(^1\text{D})$  atoms not only in the stratosphere but also in the troposphere down to ground level. Then excited atoms which are not quenched by  $\text{N}_2$  and  $\text{O}_2$  will produce NO molecules by reaction with  $\text{N}_2\text{O}$  and OH radicals by reaction with  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{H}_2$  in the troposphere and stratosphere.



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Table I: Photolysis of  $O_3-N_2O$  Mixtures at 3130Å and 25°C

<u><math>[O_3]</math>, Torr</u>	<u><math>[N_2O]</math>, Torr</u>	<u><math>\phi\{N_2\}</math></u>	<u><math>\phi\{O(^1D)\}^a</math></u>
8.7	520	0.273	0.53
17.5	430	0.200	0.48
27.5	520	0.215	0.52
33.8	490	0.172	0.45
			Ave. = $\overline{0.50} \pm 0.03$

a) calculated from Eqn. I.

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